Self-assembly of discotic liquid crystalline molecule-modified gold nanoparticles: control of 1D and hexagonal ordering induced by solvent polarity†

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Gold nanoparticles fully coated with discotic liquid crystalline molecules of hexaalkoxy-substituted triphenylene (Au–TP) have been synthesised, the self-assembled structure of which could be controlled (hexagonal or 1D nanochain) just by altering the ratio of methanol to toluene in the solvent.

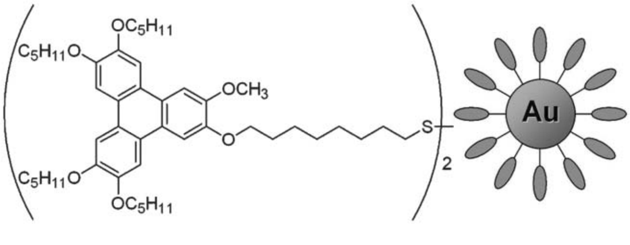
Recently, several studies related to the construction of highly-ordered metal nanoparticle assemblies have been reported.[1] From the viewpoint of electronic energy transport[2] and optical devices,[3] researchers have focused on the one-dimensional (1D) arrangement of nanoparticles. The decrease in interparticle spacing can elicit a dramatic increase in particle–particle electronic interaction, leading to an efficient 1D tunneling current and a potential role as nanowires.[4] The development of the 1D assembly technique is hard to achieve, as it is unsuited to hexagonal closed packed (hcp) structures because of their low-symmetric structural isotropy. Existing methods for fabricating a 1D arrangement of non-magnetic particles include the use of electron beam lithography,[5] templates[6] and the self-assembly of nanoparticles.[7]

In this study, the secret is to introduce discotic liquid crystal molecules, hexaalkoxy-substituted triphenylene (TP),[8] into an organic ligand surrounding a gold nanoparticle surface (Au–TP). We considered that the TP molecules were self-assembled into 1D columnar mesophase *via* π–π interactions,[9] expecting that the adoption of TP molecules would be a strong trigger for the 1D assembly of metal cores. Moreover, a Au–TP superlattice could be intentionally altered just by tuning the extent of the π–π interactions amongst the TP moieties in solvents of various polarity. We first present the preparation of gold nanoparticles stabilized by TP ligands with a thiol group [8-(3-methoxy-6,7,10,11-tetrakis-pentyloxy-triphenylen-2-yloxy)-octanyl disulfide, TPD, see Scheme 1]. Next, we show how the practical control of the Au–TP assembly between 1D and hcp ordering can be induced by the solvent selected, dependent on the extent of the interparticle interactions among the neighboring Au–TPs. Specifically, the fluorescence (FL) spectra reveal that during the Au–TPs' assembly mechanism the dynamics of the π electron overlap amongst the TP units *in solution* affects the assembled structure.

TPD was newly prepared *via* several stepped reactions (ESI, Scheme S1†) with a total yield of 56.5%. Au–TP with different core diameters was synthesized in a homogeneous reduction in DMF–water. Briefly, 1 mL of 10 mM aq. $HAuCl_4$ and 40 mL of DMF were added to x mL of 1 mM TPD in DMF [x = 5 (Au-TP1), 2 (Au-TP2), and 1 (Au-TP3)]. After heating to 60 °C, 1 mL of 0.1 M aq. $NaBH_4$ was introduced to the mixture with 2 h of vigorous stirring. 40 mL of water was added, then, the solution was extracted with 20 mL of toluene. The separated toluene phase was washed with 10 mL of water, and the solid was precipitated by the addition of methanol. This precipitation process was repeated 3 times, followed by excess washing with methanol to give a black powder of Au–TPs. As for the TEM measurement of Au–TP, 2 droplets ($\sim$0.05 mL) of the prepared Au–TP solution (10^{-5} g mL^{-1}) aged for 2 days were dropped on to the carbon-supported copper grid, and dried naturally for 1 day before the measurement.

The dispersibilty of the prepared Au–TPs was very high in various organic solvents, such as hexane, toluene, chloroform, THF, acetone, and DMF. From the TEM images (Fig. S1† and Fig. 1a), it can be seen that the mean diameter of Au–TP, d_{av}, was controllable from 2.4 to 3.0 nm (with a small standard deviation) by changing the molar ratio of TPD : Au in the reaction mixture (Table 1). The ^1H NMR spectra of Au–TP in $CDCl_3$ exhibited broadened signals, assigned to the surrounding TP ligands, due to dipolar spin relaxation on the Au particle surface (Fig. S2†).[10] Note that the chemical shift of the protons in the triphenylene and methoxy groups of the TP unit dramatically move more upfield after modification of the particle surface (Table S1†), which suggests a stronger stacking interaction among the packed TP moieties on the particle surface than in a free molecule.[11] No contamination of the free TPD ligands was confirmed by ^1H NMR signals.

Fig. 1 shows the TEM images of the Au–TP1 assemblies prepared in a mixture of a polar (methanol) and a less polar



Scheme 1 Left: Structure of TPD. Right: Schematic representation of Au–TP.

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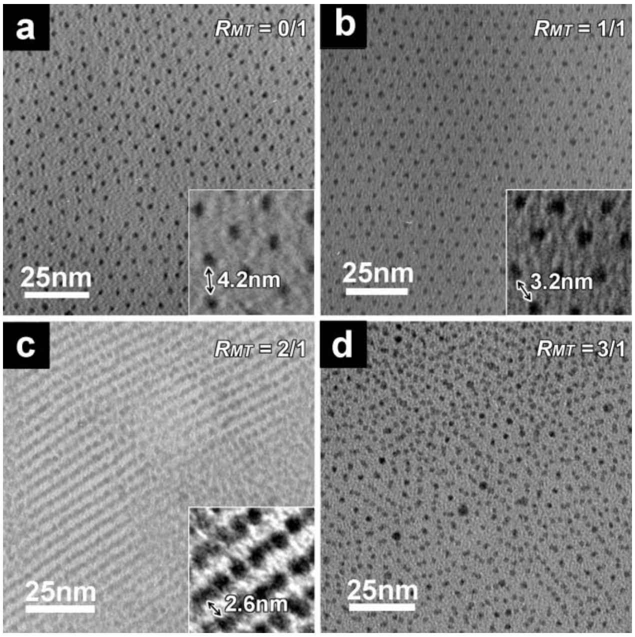

Fig. 1 TEM images of Au–TP1 prepared in a ratio of methanol to toluene (v/v) of (a) 0 : 1, (b) 1 : 1, (c) 2 : 1, and (d) 3 : 1. The inset shows the enlarged image.

(toluene) solvent. We strictly control the solvent polarity by altering the mixed ratio of methanol to toluene (v/v), R_{MT}, from 0 : 1 to 3 : 1. The R_{MT} value is regarded as a kind of polarity index. When the solvent polarity is relatively low (R_{MT} = 0 : 1, 1 : 1), a clear hcp structure is formed with a particle spacing, d_{int}, of 4.2 and 3.2 nm, respectively (Fig. 1a and 1b). The full molecular length of the TP ligand is *ca.* 2.4 nm calculated by MOPAC described in Fig. 2d, where the C8 alkyl chain is 1.1 nm, the aromatic frame of the TP moiety is 0.6 nm, and the surrounding pentyloxy group of the TP moiety is 0.7 nm. These values indicate that the Au–TP1 in Fig. 1a self-assembled by intercalating only the adjacent pentyloxy moiety around the TP ligands (Fig. 2a). On the other hand, those in Fig. 1b should accompany a *partial* π–π interaction of the TP units (Fig. 2b).

Interestingly, when the polarity of the solvent was further increased to R_{MT} = 2 : 1, the assembled structure was entirely converted from hcp to a 1D arrangement (Fig. 1c). The interparticle spacing in a chain is *ca.* 0.7 nm. The row spacing, d_{row}, is 2.6 nm, a value which is consistent with the *full* stacking of the TP units interdigitated among the adjacent Au–TP particles (Fig. 2c). The ordering status of the 1D chain is significantly developed compared to the existing nanoparticles stabilized by a typical nematic liquid crystalline molecule.[7] This finding suggests that the 1D stacking ability of discotic liquid crystalline molecules is very powerful. The well-defined superstructure of Au–TP1 disappears with an increase of R_{MT} above 3 : 1 (Fig. 1d).

To understand the assembly mechanism, the FL spectrum of the Au–TP1 solution in methanol–toluene was assessed at 0 h and 48 h, as shown in Fig. 3. With increasing time, a significant enhancement of the FL intensity at 412 and 438 nm could be identified only for R_{MT} = 1 : 1 and 2 : 1 (Fig. 3b and 3c), while it was hardly observed for R_{MT} = 0 : 1 and 3 : 1 (Fig. 3a and 3d). Additionally, the intensity increase for R_{MT} = 2 : 1 (Fig. 3c) is more conspicuous than that for R_{MT} = 1 : 1 (Fig. 3b). Considering that the emissions at 410–440 nm are attributed to the conventional staggered or helical π-electron overlapping mode of the TP molecules,[12] these FL data imply that the TP units on a particle surface are gradually intercalating among neighboring

Table 1 Influence of the molar ratio of TPD to Au in a reaction mixture on the mean diameter (d_{av}) and the standard deviation (σ) of Au–TP

Compound	TPD/Au (mol/mol)	d_{av}/nm	σ/nm
Au–TP1	0.5	2.4	0.3
Au–TP2	0.2	2.8	0.4
Au–TP3	0.1	3.0	0.3

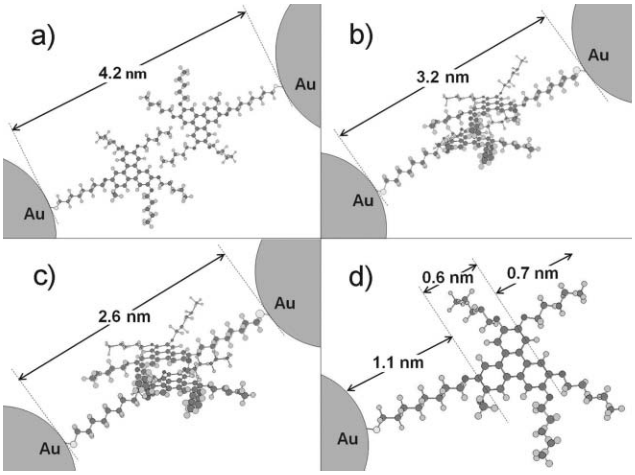

Fig. 2 Schematic illustration of (a) adjacent TP ligands on a gold core surface with non-stacking (d_{int} = 4.2 nm), (b) with partial stacking (d_{int} = 3.2 nm), (c) with full stacking (d_{row} = 2.6 nm) of TP units, and (d) a single TP ligand on a gold core surface.

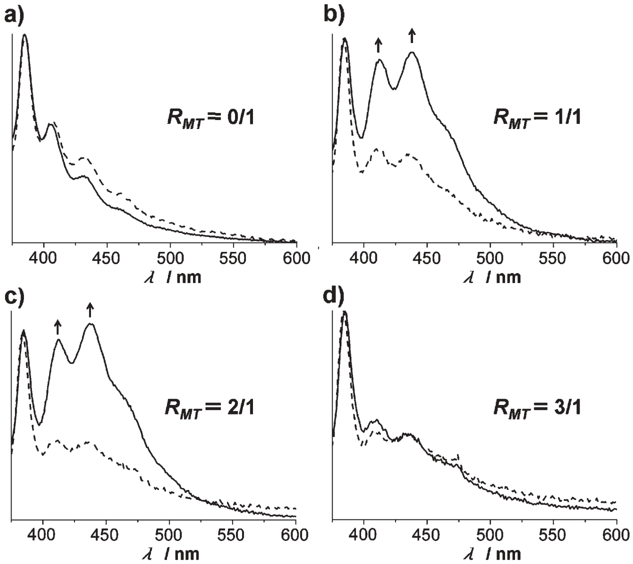

Fig. 3 Fluorescence spectral change of 1.0×10^{-5} g mL^{-1} Au–TP1 in methanol–toluene with (a) R_{MT} = 0 : 1, (b) 1 : 1, (c) 2 : 1 and (d) 3 : 1 at 0 h (dotted line) and 48 h (solid line). Fluorescence excitation is at 345 nm.

particles, and that they produce *inter*particle π–π electronic stacking among the neighboring Au–TPs. This elucidation is quite consistent with the TEM observations and MOPAC calculations. Namely, it is reasonably interpreted that the TP units generate π electronic stacking among particles most frequently with R_{MT} = 2 : 1 to give a 1D assembly with *fully*-overlapped TP moieties (Fig. 1c and 2c). In the same way, the TP moieties are secondarily inclined to be stacked with R_{MT} = 1 : 1, leading to hcp ordering with *partially*-overlapped TP moieties (Fig. 1b and 2b).

In order to elucidate the assembly mechanism more precisely, we should also notice that the hcp arrangement of Au–TP can not be obtained for R_{MT} = 3 : 1 (Fig. 1d), but it is apparently formed for R_{MT} = 0 : 1 (Fig. 1a), even though the interparticle π– π interaction of the TP units does not seem to work in either of the cases. The reason for this ordering difference is plausibly due to the lower dispersibilty of Au–TP in methanol than in toluene. When the powdery Au–TPs are introduced into a solvent with R_{MT} = 3 : 1, the TP ligands on the metal core surface are not well-solvated, *i.e.*, they are not rearranged sufficiently to generate the effective intercalation among the pentyloxy groups of the TP moieties, leading to a failure to construct the hcp assembly as happens for R_{MT} = 0 : 1. A suitable ratio of the mixed solvent which triggers the well-defined ordering of Au–TP might be determined by the parametric balance among the physical properties, *e.g.* metal core size, alkyl chain length of the TP ligand.

From these findings, we can deduce that the interparticle π–π interaction of the TP units in solution is inevitable for the 1D arrangement of Au–TP, while that interaction is supportive, but not indispensable for the hcp ordering of Au–TP. Strictly speaking, Au–TP assembly *in solution* and *on a substrate* proceeds under different conditions, because the latter occurs with the evaporation of solvent molecules. However, from the concrete results, we claim that the interactive status in solution is carried over during the solvent evaporation process, accompanied by attractive capillary forces, strongly acting on the assembly morphology of the nanoparticles even on a substrate.

Finally, there is one interesting point left: why can Au–TP order linearly in a solvent where the *inter*particle π–π interaction of the TP units is dominant? This is necessarily attributed to the specific nature of the TP ligands: discotic liquid crystalline molecules tend to gather into a 1D column.[9] When the *inter*particle π–π stacking is promoted in an appropriate mixed solvent (here R_{MT} = 2 : 1), the small columnar phase of the TP units will be constructed by the intercalation of TP ligands among the Au–TPs. During the ordering process of the collected TP columnar phase, the partial area on a metal core surface, where protection by TP ligands becomes weak due to alkyl chain bending of the TP ligands, turning of the TP column direction is inevitably produced. Consequently, the van der Waals attraction among the metal cores is accelerated, causing the gradual aggregation of Au–TPs. At that time, the specific 1D nucleus of the Au–TPs is compulsorily constructed on account of the surrounding TP column, resulting in the secondary growth of the 1D Au–TP arrays through directional motion of nanoparticles toward the ordered arrays, accompanied by the solvent evaporation process. The investigation of other solvent impact parameters, *e.g.*, molecular structure, bolting point, *etc.* is under way in our laboratory, simultaneously with the consideration of the dependence of the assembled structure of Au–TPs on their physical properties (core size, alkyl chain length of the TP ligand).

In summary, we have synthesised gold nanoparticles functionalized by hexaalkoxy-substituted triphenylene (TP) as a discotic liquid crystalline molecule (Au–TP). The self-assembled structure of Au–TP could be controlled (1D or hexagonal closed packed (hcp) structures) by the ratio of the solvent used (methanol–toluene), triggered by the extent of the π–π interactions among the adjacent TP ligands on a particle surface. We have presented the distinct phenomenon that the gathering status of the surrounding organic ligands themselves *in solution* influence the self-assembled structure of metal nanocores on a substrate. This finding is fundamental to nanoscience, and is applicable to the excellent design of other organic–inorganic nanoparticles as well. Our ultimate goal is to create a novel electronic transportation system provoked by the combination of metal nanoparticles and the TP molecules. Concomitantly, we expect that the electrophilic properties of the prepared Au–TP assembly will potentially possess versatile applications in electronic and optical nanodevices, *e.g.*, organic light-emitting diodes, field effect transistors, and electroluminescence.

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